

## REMARKS

By the present amendment, applicant is limiting the claimed polymers to Nylon 12 and PET and the nanocomposite to nano-tubes and nano ceramic fibers.

Nylon 12 is commonly known as a homo-polymer and is not a nylon block copolymer. Clearly Nylon 12 and PET are different than block Nylon block copolymer as called for in the Acquarulo WO 01/34685.

Further the Acquarulo publication is limited to nano clays which react with the polymer, that is to say, the nano clays are reacted with the polymer matrix and nano-tubes are not. The nano-tubes or nano ceramic fibers are added to the polymer matrix as a nanoreinforcement agent due to their strength. Further, the nano size is ideal to be used in thin films where high temperature processing is required (extrusion). A gross comparison would be adding glass fiber to polyester (fiberglass). Still further, carbon nanotubes achieve a high oxidation state, carbon is very stable and remains an independent entity within the polymer matrix.

Applicant makes reference to a commercial product called **Nanocor™**. Enclosed is a website printout concerning Nanocor products and patents, information on nano and polymer composites as well as a glossary of terms that further define the difference between a passive filler (carbon nano particles) and an active chemical (nanoclays).

The Examiner's rejection of claims 1-25 for being anticipated by the Acquarulo et al., Published Application US 2003/0229184, as this rejection may be attempted to be applied to the amended claims, is respectfully traversed.

In support of this traverse, applicant points out that the polymers now called for in the claims, namely Nylon 12 and PET are not disclosed in or suggested by Acquarulo which calls for nylon block copolymers. Nylon 12 and PET are not commonly known as being block copolymers. Applicant does not teach the use of Nylon block copolymers and the ordinary meaning of Nylon 12 and PET does not include they being block copolymers.

Note that Acquarulo states:

“the present invention also relates to a balloon type catheter having a tubular shaft comprising a nylon *block copolymer* and a nano clay filler, including a compound which promotes crosslinking therein, the improvement comprising *irradiation crosslinking said nylon block copolymer* of the balloon section.” (Emphasis added – page 6, lines 7-11)

Additionally, claims 7-9 of Acquarulo spell out the types of block copolymers he is referring to.

Further, as the Examiner has noted, Acquarulo does not teach or suggest nano-tubes or nano ceramic fibers, now called for in all the remaining claims. The Examiner has contended that there is no difference between nano clays and nano-tubes or nano ceramic fibers. This is not true since the smectite clay family in which nano clays are found are reacted with the polymers in Acquarulo's matrix. This is clearly brought out by Acquarulo's teaching of the use of crosslinking agents and preferably the use of radiation. As, clearly stated by Acquarulo:

“the nano clay may be combined with another chemical ingredient, such as a crosslinking agent, to thereby provide a unique synergistic effect on mechanical property performance.” (page 1, lines 4-7)

Further, Acquarulo states:

“it has been found herein that upon incorporation of a crosslinking promoter, the effect of the nano clay is enhanced, in the sense that a synergy is observed between the promoter and the nano clay on mechanical properties.” (page 5, lines 24-27)

The synergy is an increase in the flexural modulus, which increases the rigidity of a tubular shaft of a balloon catheter.

Applicant provides nano tubes or nano ceramic fibers in a polymer matrix to reinforce the matrix to obtain a stronger balloon in a balloon catheter and does not teach reacting a nano clay with a crosslinking compound and Nylon block copolymers to increase the flexural modulus.

Applicant does not react the polymer with the nano-tubes or nano ceramic fibers using a cross linking agent and applicants resulting reinforced polymer matrix comprises different ingredients than the Acquarulo polymer matrix.

Further, applicant orients the nano-tubes or nano ceramic fibers in the formation of his balloon. Acquarulo does not at all teach or suggest orientation of his nano clay particles.

Accordingly, applicant submits that the claimed balloon is different than and not obvious from the teachings of Acquarulo and is made with a method different than the Acquarulo method.

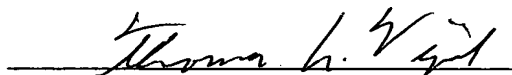
In summary, for the reasons set forth above, the balloon catheter now defined even more clearly in the amended claims is novel and not obvious from the teachings of Acquarulo.

An earnest endeavor has been made to place this application in condition for allowance, and an early and favorable action to that end is requested.

Respectfully submitted,

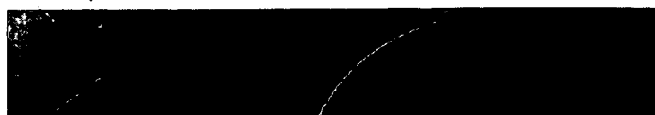
June 1, 2005

Date



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**REPORT**

[Report]

## **Polymer Nanocomposites: Nanoparticles, Nanoclays and Nanotubes**

Pub Time: 2004/03

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### **INTRODUCTION**

#### **STUDY GOALS AND OBJECTIVES**

This report focuses on polymer nanocomposites and their uses. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications already can be found in the marketplace.

For decades, mineral fillers, metals and fibers have been added to thermoplastics and thermosets to form composites. Compared to neat resins, these composites have a number of improved properties including tensile strength, heat distortion temperature and modulus. Thus for structural applications, composites have become very popular and are sold in billion-pound quantities. These filled thermoplastics are sold in even larger volumes than neat thermoplastics.

Furthermore, the volume of fillers sold roughly equals the volume of thermoplastic resin sold. Clearly, the idea of adding fillers to thermoplastics and thermosets to improve properties, and in some cases decrease costs, has been very successful for many years.

Thermoplastics have become part of the fabric of modern life. Billions of pounds of these materials are sold annually, and the rate of thermoplastic production is increasing. These materials are ubiquitous and found in homes, cars, offices, and a host of other places. Thermoplastics have grown in acceptance in our society because they perform well for their cost.

More recently, advances in synthetic techniques and the ability to characterize materials readily on an atomic scale have lead to interest in nanometer-size materials, e.g., grains, fibers and plates. They have dramatically increased surface area compared to conventional-size materials, and the chemistry of nanosize materials is altered in comparison to conventional materials.

Polymer nanocomposites combine composites and nanometer size



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materials. Thermoplastics filled with nanometer size materials have properties different from thermoplastics filled with conventional materials. Some of these properties, such as increased tensile strength, may be achieved by using higher conventional filler loading at the expense of increased weight and decreased gloss. Other properties, such as clarity or improved barriers, cannot be duplicated by filled resins at any loading.

Polymer nanocomposites were developed in the late 1980s by both commercial research organizations and academic laboratories. Toyota was the first company to commercialize these nanocomposites, and it used nanocomposite parts in one of its popular models for several years. Following Toyota's lead, a number of other companies also began investigating nanocomposites.

Most of the commercial interest in nanocomposites has been focused on thermoplastics. They can be broken into two groups: less expensive commodity resins and the more expensive (and higher performance) engineering resins. One of the goals of nanocomposites was to permit substitution of more expensive engineering resins with a less-expensive commodity resin nanocomposite. Substituting a nanocomposite commodity resin with equivalent performance as a more expensive engineering resin should yield overall cost savings.

Using a strict definition of nanocomposites, i.e., any filler submicron in size, there already are significant volumes of nanocomposites being produced (probably more than 100 million pounds). However, the fillers, carbon black, fumed silica and calcium carbonate, do not alter the performance of the composite dramatically when compared to conventional size fillers. Furthermore, these materials have been known and used for decades. Often, particles used in composites are agglomerates of smaller particles. This was unknown until microscopy developed to the point where it could characterize these particles more fully.

Much of the research interest in nanocomposites was jump-started by the National Nanotechnology Initiative (NNI). More research money was provided by this initiative than was spent on the Human Genome Project. For example, NNI funding exceeded \$600 million in 2003 and continues to increase.

The goals of the NNI have been adopted by many nanotechnology researchers (who are looking for funding, of course):

1. Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1 nanometer to 100 nanometer range.
2. Creating and using structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.
3. Ability to control or manipulate on the atomic scale; nanotechnology implies that new materials and applications are being developed to specifically exploit the properties found in this size range.

Consequently, this report excludes composites made from conventional materials, even if they are composed of particles that meet the strict dictionary size definition of nanoparticles.

At this point in time, there has been much less open commercial interest in thermoset nanocomposites compared to thermoplastics. Yet thermoplastics have been able to dominate a major coating market in a relatively short time frame.

Nanocomposites have proven to be more difficult to manufacture than first anticipated, but new materials in pilot plants and laboratories may be able to live up to much of their initial promise. Greater understanding of the chemistry driving the formation of nanocomposites has enabled researchers to discover practical production methods for these materials.

Nanocomposites offer improvements in several of the properties of thermoplastics including tensile strength, modulus, barrier and heat distortion temperature. If a nanocomposite could offer these improvements at no additional cost, then it quickly would replace a large percentage of unfilled thermoplastics. Unfortunately, improved performance of a nanocomposite compared to a thermoplastic comes with an increase in price.

Therefore, replacement will not come on a wholesale basis, but will take place in applications where improved performance of a nanocomposite justifies the price increase. Nanocomposites are not going to be commodity materials. They are specialty materials that will carry a price premium for the foreseeable future.

Since nanocomposites will not completely replace any particular unfilled resin, over the next 5 years, amounts of nanocomposites will be modest by thermoplastic standards. However, nanocomposites already are produced in multimillion-pound quantities and these applications should increase dramatically during the next half-decade.

This report summarizes and describes current nanocomposite products, and covers some of the future developments involving these materials. It also covers a number of applications for these nanocomposites, and estimates possible future markets for them.

Armed with this information, readers with business interests then can make sound judgments regarding marketing strategies, investment decisions, or strategic plans concerning markets for polymer nanocomposites. This report was written to be readily accessible for readers with a business background, but accuracy concerning the technical aspects of polymer nanocomposite manufacture has not been sacrificed.

## **REASONS FOR DOING THE STUDY**

While there has been considerable ballyhoo in the popular press regarding the wonders of polymer nanocomposites, it is difficult to get solid information on how many of these nanocomposites are being produced and sold. Furthermore, many articles have presented wildly misleading

information concerning the manufacture, markets and applications of these materials. This report offers a timely picture of trends in polymer nanocomposites that cannot be obtained from other sources.

### **CONTRIBUTION OF THE STUDY**

This report discusses the current and future sizes of the polymer nanocomposite market on a global basis. The U.S. is, and probably will remain, the dominant producer and one of the world's largest markets for polymer nanocomposites. Thus, there is a heavy focus on trends in this country.

Readers of this report will be able to distinguish the hype concerning the uses of polymer nanocomposites from the reality of the market. A number of potentially significant markets for polymer nanocomposites have received relatively little press, and many of the published articles concerning uses of these materials do not provide an accurate picture.

### **SCOPE AND FORMAT**

To generate the information required to construct a reasonable future market for polymer nanocomposites, it is necessary to take a hard look at the potential advantages and pitfalls of the current crop of these materials as compared to conventionally filled polymers. This report does not delve into the likelihood of exotic new forms of transportation. Instead, it is restricted to the possible replacement of existing conventional materials with polymer nanocomposites. Possible applications of nanocomposite materials within the next 5 years also are discussed.

This report features two types of polymer nanocomposites:

- Thermoplastic: these materials are broken into two major categories, i.e., commodity resins and engineering resins; the potential of polymer nanocomposite commodity resin is covered by filler types such as nanoclays, nanotubes and metal oxides.
- Thermoset nanocomposites: these have received less commercial interest during their development than have thermoplastic nanocomposites, but the materials have been more straightforward to produce.

The report is broken into five sections. First there is a technology overview that gives the broad details of polymer nanocomposites, along with some of their physical properties and methods of manufacture. Next there is an extensive description of the industry that is developing polymer nanocomposites including clay manufacturers, nanotube manufacturers, metal oxide filler manufacturers, thermoplastic resin producers, and compounders, along with company profiles. The products section covers nanocomposites by filler type, along with relevant resins for each nanocomposite. The report concludes with a market applications section that covers the likely trends over the next 5 years.

### **METHODOLOGY AND INFORMATION SOURCES**

This report is the end result of 4 months of concerted effort by the author. Primary information sources were interviews with several dozen people in industry, academe and the government. The author also attended meetings and conferences, and much precious insight was gained from these sources as well. Many of the people interviewed are recognized authorities in the field, and provided invaluable assistance. I would like to thank all who took the time to speak with me for their help with this project.

Since this study was not commissioned by any corporation or individual, the author's brief in writing it was to be as objective as possible.

Secondary sources used for this report include a number of publications issued by the federal government, as well as items from the Internet, corporate literature and peer-reviewed literature.

Any time an estimate of a number is made, the underlying assumptions are discussed. Thus, if a reader chooses to interpret raw data in a different way, it is possible to do so. Dollar amounts are in constant 2003 dollars, and average annual growth rates (AAGRs) are calculated using standard tables.

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## Glossary

A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V | W | X | Y | Z

**cation:** a positively charged ion.

**clay-chemical complex:** an intimate association of montmorillonite clay and an intercalant (surface treatment), wherein the intercalant ionically bonds to the clay surface. The association creates a material which is compatible with host resins, permitting montmorillonite to disperse in them.

**compatibilization:** the process of surface modifying a nanoclay so that it is attracted to and will disperse in resin matrices. The two most common compatibilization classes are onium ion modification and ion-dipole interaction.

**exfoliate:** a noun, used in patent literature to describe a surface treated nanoclay, which possesses a sufficiently enlarged gallery spacing to permit the nanoclay to fully disperse (exfoliate) in a plastic matrix.

**exfoliation:** a process wherein packets of nanoclay platelets separate from one another in a plastic matrix. During exfoliation platelets at the outermost region of each packet cleave off, exposing more platelets for separation. Nanoclay compatibilization is essential for exfoliation.

**gallery:** space between parallel layers of montmorillonite clay platelets. The gallery spacing changes depending on what molecule or polymer occupies the space.

**hydrophilic:** a chemical environment favoring the attraction of water or materials which are miscible in water. Hydrophilic materials are characterized by strong dipole moments. They are basically immiscible with organophilics.

**Imperm®:** an ultra high barrier nanocomposite plastic which features enhanced barrier to gases, water vapor and hydrocarbon fuels. Product of Mitsubishi Gas Chemical, Inc - Nanocor Alliance.

**intercalant:** an organic or semi-organic chemical capable of entering the montmorillonite clay gallery and bonding to the surface.

**intercalate:** a clay-chemical complex wherein the clay gallery spacing has increased, due to the process of surface modification. Under the proper conditions of temperature and shear, an intercalate is capable of exfoliating in a resin matrix.

**interlayer space:** the space between individual nanoclay platelets. It varies, depending on the type of molecules that occupy the space. Also known as "gallery space."

**ion-dipole interaction:** a type of chemical bond formed between a charged ion and a molecule that contains a dipole moment and a partial localized negative charge. A classic example is water of hydration in many compounds. The complex has a definite ratio of organic or polymer to clay.

**masterbatches/concentrates:** plastic resin pellets which contain high loadings (40-50%) of nanoclay in partially dispersed form. Masterbatches/concentrates can be letdown with additional resin to form nanocomposites with nanoclay loadings of 4-6%.

**montmorillonite clay:** the most common member of the smectite clay family. Montmorillonite is generally referred to as "nanoclay". It is also the most common material used in plastic nanocomposites.

**nanoclay:** a clay from the smectite family. Smectites have a unique morphology, featuring one dimension in the nanometer range.

**nanocomposites:** new class of plastics derived from a highly refined form of nanoclay that disperses in plastic resins. These nano-sized particles are composed of montmorillonite minerals.

**nanocomposite technology:** the materials and processes required to disperse nanoscale particles in plastics, metals, or ceramics.

**Nanomer® nanoclays:** surface modified montmorillonite clays, or masterbatches containing modified clays, that are utilized to make a nanocomposite. Nanomer nanoclays may be generically referred to as "intercalates" in patent literature.

**nanometer:** a unit of measure. One nanometer corresponds to a length which is one-billionth of a meter, or about one ten-thousandth the diameter of a human hair.

**onium ion modification:** the formation of a clay-chemical complex using an intercalant (surface treatment) containing an ammonium or phosphonium functional group. The groups modify a nanoclay surface by ionically bonding to it, converting the surface from a hydrophilic to an organophilic species.

**organophilic:** a chemical or molecular orientation favoring the attraction of hydrocarbons or materials which are miscible in hydrocarbons. Organophilic materials are characterized by weak dipole moments. They are basically immiscible in water.

**platelet:** general shape of a montmorillonite particle, consisting of a sheet-like structure where the dimensions in two directions far exceed the particle's thickness.

**thermoplastic:** plastic that softens when exposed to heat and returns to its original condition when cooled to room temperature.

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10. What is Nanocor's patent position, and how does that effect our position in the market?

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#### 1. I've heard a lot about nanocomposites, but I do not see a lot of commercial products yet, how come?

There are a limited number of commercial products currently available, and many more set to begin commercial use in the near future. Many customers, after spending time and finances to develop these superior products, are not willing to let their competitors in on their secrets.

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#### 2. Why should I use Nanomer nanoclays vs. other nano materials, such as nanotubes, or nanometals?

The products offered by Nanocor are designed specifically for the plastic industry, and have the highest level of purity of any naturally produced nanoclay product on the market today. Nanomer nanoclays are significantly more cost competitive compared to nanotubes and nanometals.

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### **3. What type of resin matrices are Nanomer nanoclays available for?**

The number continues to grow but can be broken into three main categories, polyolefins, polyamides, and engineering resins. See our [Product Lines](#) section for an expanded listing. If you have questions about your specific resin or grade, please do not hesitate to inquire.

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### **4. I am an end user; I do not have compounding capabilities. Can I take advantage of Nanomer technology?**

Absolutely. Nanocor or one of our industry partners can provide material in several forms to include concentrate and finished nanocomposite. Concentrates are available from a number of companies; [Clariant](#), [PolyOne](#), and [RTP](#) to name a few. Finished nanocomposites are also available from Nanocor or certain resin producers, such as [Honeywell](#) and [Bayer](#). Nanocor would be happy to show you how to best implement nanotechnology for your needs.

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### **5. How do I know I have reached complete dispersion?**

There are a number of tests that can be performed, but first it's important to understand that a completely exfoliated product is not always necessary to achieve your goals. Nanocor can show you how to ensure that your product is reaching its full potential, and how to perform both lab and product testing, to ensure consistent results.

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### **6. Will I need to buy special equipment, or completely overhaul my process conditions?**

One of the great benefits to processing Nanomer nanoclays is that normally there is no need to purchase special equipment, or significantly change your processing conditions. In fact in many cases Nanomer nanoclays can be easier on your equipment than other, more traditional additives.

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### **7. Can I use Nanomer nanoclays in conjunction with other fillers or additives?**

Yes. A number of applications have been developed combining our nanoclays with fiberglass and fillers such as talc or mica. However, it may be necessary to check with Nanocor technical staff to be sure there is no interaction between the surface treatment of the Nanomer nanoclays and other additives in your current formulation.

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**8. I've read a lot about the flame retardant capabilities of nanoclays; can I reach a UL V-O fire rating with Nanomer nanoclays alone?**

The simple answer is no. However, we nanoclays can help you reduce the loading level of your current FR package, achieving higher properties, lower specific gravity, and significant cost savings. Also, a number of applications are currently under development to eliminate the use of halogen-based additives, due to environmental concerns surrounding this class of flame retardants.

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**9. My application has fairly large quantity requirements; can Nanocor meet our commercial needs?**

Certainly. Nanocor currently has a production capacity of 7 million pounds of Nanomers annually, and infrastructure in place to raise capacity to well over 100 million pounds as the market needs increase.

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**10. What is Nanocor's patent position, and how does that affect our position in the market?**

Nanocor currently has 40 issued patents, primarily involving the creation of Nanomer nanoclays and Nanomer surface treatments. Nanocor purposely avoids any down stream patents, in order to not impede customers from entering the market place. Nanocor also monitors the patent field for nanocomposites, and would be happy to discuss your concerns.

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**Technical | Commercial**

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## Patents

Nanocomposite patents are owned by Nanocor's parent, [AMCOL International Corp.](#) We have been active in seeking patent protection in this field and Nanocor is the beneficial holder of over two dozen US patents. We have also routinely filed international counterparts. Our central goal in seeking patent protection is simple: making the benefits of this technology broadly available to our customers.

This section contains information in abstract form for all issued US patents.

Patent #	Title	Issue Date
<a href="#">6,596,803</a>	A Polymer Nanocomposite Comprising a Matrix Polymer and a Layered Clay Material Having a Low Quartz Content	07.22.2003
<a href="#">6,632,868</a>	Intercalates Formed with Polypropylene/Maleic Anhydride Modified Polypropylene Intercalants	10.14.2003
<a href="#">6,462,122</a>	Intercalates Formed with Polypropylene/Maleic Anhydride-Modified Polypropylene Intercalants	10.08.2002
<a href="#">6,461,423B1</a>	Intercalates and Exfoliates Formed with Hydroxyl-Functional; Polyhydroxyl-Functional and Aromatic Compounds; Composite Materials Containing Same and Methods of Modifying Rheology Therewith	10.08.2002
<a href="#">6,407,155</a>	Intercalates Formed Via Coupling Agent-Reaction And Onium Ion-Intercalation Pre-Treatment Of Layered Material For Polymer Intercalation	06.18.2002
<a href="#">6,391,449</a>	Polymer/Clay Intercalates, Exfoliates, And Nanocomposites Comprising A Clay Mixture And A Process For Making Same	05.21.2002
<a href="#">6,387,996</a>	Polymer/Clay Intercalates, Exfoliates And Nanocomposites Having Improved Gas Permeability Comprising A Clay Material With A Mixture Of Two Or More Organic Cations And A Process For Preparing Same	05.14.2002
<a href="#">6,376,591</a>	High Barrier Amorphous Polyamide-Clay Intercalates, Exfoliates, And Nanocomposites And A Process For Preparing Same	04.23.2002
<a href="#">6,339,690 B2</a>	Layered Compositions With Multi-Charged Onium As Exchange Cations, And Their Application To Prepare Monomer, Oligomer, And Polymer Intercalates And Nanocomposites Prepared With The Layered Compositions Of The Intercalates	06.04.2002
<a href="#">6,262,162</a>	Layered Compositions with Multi-Charged Onium Ions as	07.17.2001

	Exchange Cations, and Their Application to Prepare Monomer, Oligomer, and Polymer Intercalates and Nanocomposites Prepared with the Layered Compositions of the Intercalates	
<u>6,251,980</u>	Nanocomposites Formed by Onium Ion-Intercalated Clay and Rigid Anhydride-Cured Epoxy Resins	06.26.2001
<u>6,242,500</u>	Intercalates and Exfoliates Formed with Long Chain (C6+) or Aromatic Matrix Polymer-Compatible Monomeric/Oligomeric or Polymeric Intercalant Compounds, and Composite Materials Containing Same	06.05.2001
<u>6,235,533</u>	Method of Determining the Composition of a Clay Deposit	05.22.2001
<u>6,232,388</u>	Intercalates Formed by Co-Intercalation of Onium Ion Spacing/Coupling Agents and Monomer, Oligomer or Polymer MXD6 Nylon Intercalants and Nanocomposites Prepared with the Intercalates	05.15.2001
<u>6,228,903</u>	Exfoliated Layered Materials and Nanocomposites Comprising Said Exfoliated Layered Materials Having Water-Insoluble Oligomers or Polymers Adhered Thereto	05.08.2001
<u>6,225,394</u>	Intercalates Formed by Co-Intercalation of Onium Ion Spacing/Coupling Agents and Monomer, Oligomer or Polymer Ethylene Vinyl Alcohol (EVOH) Intercalants and Nanocomposites Prepared with the Intercalates	05.01.2001
<u>6,126,734</u>	Intercalates and Exfoliates Formed with Hydroxyl-Functional; Polyhydroxyl-Functional; and Aromatic Compounds; Composite Materials Containing Same and Methods of Modifying Rheology Therewith	10.03.2000
<u>6,124,365</u>	Intercalates and Exfoliates Formed with Long Chain (C6+) or Aromatic Matrix Polymer-Compatible Monomeric, Oligomeric or Polymeric Intercalant Compounds and Composite Materials Containing Same	09.26.2000
<u>6,107,387</u>	Acidified Aqueous Dispersions of High Aspect Ratio Clays	08.22.2000
<u>6,090,734</u>	Process for Purifying Clay by the Hydrothermal Conversion of Silica Impurities to a Dioctahedral or Trioctahedral Smectite Clay	07.18.2000
<u>6,083,559</u>	Intercalates And Exfoliates Formed With Hydroxyl-Functional, Polyhydroxyl-Functional, And Aromatic Compounds; Composite Materials Containing Same And Methods Of Modifying Rheology Therewith.	07.04.2000
<u>6,057,396</u>	Intercalates Formed by Co-Intercalation of Monomer, Oligomer or Polymer Intercalants and Surface Modifier Intercalants and Layered Materials and Nanocomposites Prepared with the Intercalates	05.02.2000
<u>6,050,509</u>	Method of Manufacturing Polymer-Grade Clay for Use in Nanocomposites	04.18.2000
<u>5,998,528</u>	Viscous Carrier Compositions, Including Gels, Formed with an Organic Liquid Carrier, a Layered Material: Polymer Complex, and a Di-, and/or Tri-valent Cation	12.07.1999
<u>5,952,095</u>	Intercalates and Exfoliates Formed with Long Chain (C10 +) Monomeric Organic Intercalant Compounds; and Composite Materials Containing Same	09.14.1999

<a href="#"><u>5,880,197</u></a>	Intercalates and Exfoliates Formed with Monomeric Amines and Amides; Composite Materials Containing Same and Methods of Modifying Rheology Therewith	03.09.1999
<a href="#"><u>5,877,248</u></a>	Intercalates and Exfoliates Formed with Oligomers and Polymers and Composite Materials Containing Same	03.02.1999
<a href="#"><u>5,849,830</u></a>	Intercalates and Exfoliates Formed with N-alkenyl Amides and/or Acrylate-functional Pyrrolidone and Allylic Monomers, Oligomers and Copolymers and Composite Materials Containing Same	12.15.1998
<a href="#"><u>5,844,032</u></a>	Intercalates and Exfoliates Formed with Non-EVOH Monomers, Oligomers and Polymers; and EVOH Composite Materials Containing Same	12.01.1998
<a href="#"><u>5,830,528</u></a>	Intercalates and Exfoliates Formed with Hydroxyl-Functional; Polyhydroxyl-Functional; and Aromatic Compounds; Composites Materials Containing Same and Methods of Modifying Rheology Therewith	11.03.1998
<a href="#"><u>5,804,613</u></a>	Intercalates and Exfoliates Formed with Monomeric Carbonyl-Functional Organic Compounds, Including Carboxylic and Polycarboxylic Acids; Aldehydes; and Ketones; Composite Materials Containing Same and Methods of Modifying Rheology Therewith	09.08.1998
<a href="#"><u>5,760,121</u></a>	Intercalates and Exfoliates Formed with Oligomers and Polymers and Composite Materials Containing Same	06.02.1998
<a href="#"><u>5,721,306</u></a>	Viscous Carrier Compositions, Including Gels, Formed with an Organic Liquid Carrier and a Layered Material:Polymer Complex	02.24.1998
<a href="#"><u>5,698,624</u></a>	Exfoliated Layered Materials and Nanocomposites Comprising Matrix Polymers and Said Exfoliated Layered Materials Formed with Water-Insoluble Oligomers and Polymers	12.16.1997
<a href="#"><u>5,578,672</u></a>	Intercalates; Exfoliates; Process for Manufacturing Intercalates and Exfoliates and Composite Materials Containing Same	11.26.1996
<a href="#"><u>5,552,469</u></a>	Intercalates and Exfoliates Formed with Oligomers and Polymers and Composite Materials Containing Same	09.03.1996

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**WO 01/34685 A1**

(54) Title: OPTIMIZING NANO-FILLER PERFORMANCE IN POLYMERS

(57) Abstract: A polymer composite comprising a polymer matrix having, dispersed therein, a nano clay in combination with a crosslinking promotor. In method form, the invention relates to a process for enhancing the mechanical properties of a polymer composite, comprising supplying a polymer matrix, combining the matrix with a nano clay and a crosslinking promotor and crosslinking.

1                   OPTIMIZING NANO-FILLER PERFORMANCE  
2                   IN POLYMERS

3           The present invention relates to nano clays for use in  
4 thermoplastic/thermoset polymer materials, wherein the nano clay may be  
5 combined with another chemical ingredient, such as a crosslinking agent, to  
6 thereby provide a unique and overall synergistic effect on mechanical  
7 property performance.

8           Polymer composites comprising a polymer matrix having one or more  
9 additives such as a particulate or fiber material dispersed throughout the  
10 continuous polymer matrix are well known. The additive is often added to  
11 enhance one or more properties of the polymer. Useful additives include  
12 inorganic layered materials such as talc, clays and mica of micron size.

13          A number of techniques have been described for dispersing the  
14 inorganic layered material into a polymer matrix. It has been suggested to  
15 disperse individual layers, e.g., platelets, of the layered inorganic material,  
16 throughout the polymer. However, without some additional treatment, the  
17 polymer will not infiltrate into the space between the layers of the additive  
18 sufficiently and the layers of the layered inorganic material will not be  
19 sufficiently uniformly dispersed in the polymer.

20          To provide a more uniform dispersion, as described in U.S. Pat. No.  
21 4,889,895 sodium or potassium ions normally present in natural forms of  
22 mica-type silicates and other multilayered particulate materials are exchanged  
23 with organic cations (e.g., alkylammonium ions or suitably functionalized  
24 organosilanes) thereby intercalating the individual layers of the multilayered  
25 materials, generally by ionic exchange of sodium or potassium ions. This  
26 intercalation can render the normally hydrophilic mica-type silicates  
27 organophilic and expand its interlayer distance. Subsequently, the layered  
28 material (conventionally referred to as "nanofillers") is mixed with a monomer  
29 and/or oligomer of the polymer and the monomer or oligomer polymerized.

1 The intercalated silicate is described as having a layer thickness of 7 to 12  
2 [Angstrom] and an interlayer distance of 30 [Angstrom] or above.

3 In WO 93/11190, an alternative method for forming a composite is  
4 described in which an intercalated layered, particulate material having  
5 reactive organosilane compounds is dispersed in a thermoplastic polymer or  
6 vulcanizable rubber. Yet additional composites containing these so-called  
7 nanofillers and/or their methods of preparation are described in U.S. Pat.  
8 Nos. 4,739,007; 4,618,528; 4,528,235; 4,874,728; 4,889,885; 4,810,734; 4,889,885;  
9 4,810,734; and 5,385,776; German Patent 3808623; Japanese Patent J02208358;  
10 European Patent applications 0,398,551; 0,358,415; 0,352,042; and 0,398,551;  
11 and J. Inclusion Phenomena 5, 473 (1987); Clay Minerals, 23, (1988), 27; Polym.  
12 Preprints, 32 (April 1991), 65-66; Polym. Prints, 28, (August 1987), 447-448;  
13 and Japan Kokai 76,109,998.

14 Nano clay fillers are also available based on tiny platelets of a special  
15 type of surface modified clay called montmorillonite. These surface  
16 treatments have been aimed for use with nylon-6 and polypropylene. The  
17 two manufacturers in the United States, Nanocor and Southern Clay  
18 Products, both point to increases in flexural modulus, heat distortion  
19 temperature and barrier properties.

20 Furthermore, attention is hereby directed to U.S. Patent Nos. 5,993,415  
21 and 5,998,551 which, although not relating to nano clay fillers, describe the  
22 use of crosslinking promoters to improve properties of a thermoplastic  
23 material, and, as to be discussed below, are relevant to the present invention.  
24 Accordingly, the teachings of these patents are incorporated by reference.

25 In sum, therefore, even with the numerous described composites and  
26 methods, it still remains desirable to have an improved composite and  
27 method for forming polymer composites derived from a multilayered  
28 additive (nano clays) to thereby create composites having improved  
29 properties over the polymer on its own.

1       Accordingly, it is an object of this invention to explore the suitability of  
2 combining the nano clays with an additional chemical component to establish  
3 whether or not the observed mechanical properties of a thermoplastic host  
4 resin are improved beyond the use of only a nano clay filler.

5       More specifically, it is an object of this invention to combine nano clays  
6 with a suitable crosslinking promotor, and to establish a synergistic effect of  
7 such promotors with the nano clay on the mechanical properties of a host  
8 thermoplastic matrix.

9       In addition, it is an object of this invention to apply the nano clays and  
10 additional chemical component described above (promotor) to develop an  
11 improved method to prepare materials suitable for use in medical product  
12 applications, such as balloon catheters and catheter shaft production.

13       By way of summary, the present invention comprises a composite  
14 comprising a polymer matrix having, dispersed therein, a nano clay in  
15 combination with a crosslinking promotor. By use of the term "nano clay" it  
16 is noted that such clays are inorganic minerals which have a high aspect ratio  
17 with at least one dimension of the particles therein in the nanometer range.  
18 By use of the term, "crosslinking promotor" it relates to any chemical  
19 compound that will promote crosslinking between those polymer chains that  
20 comprise the polymer matrix. Accordingly, it can be appreciate that  
21 "crosslinking promotors" include those functionalized chemical compounds  
22 that provide the requisite activity, upon activation (irradiation or heat) to  
23 chemical react and bond with the polymer chains to form covalent crosslinks  
24 between the surrounding polymer chains.

25       Preferably, the crosslinking promotor is trallylisocyanurate or  
26 trallylcyanurate, although those skilled in the art will recognize that other  
27 types of crosslinking promotors would be suitable and would fall within the  
28 broad aspects of this invention. In addition, preferably, the promotor is

1 present in the polymer matrix at a level of about 0.5% to 10% (wt.), and at any  
2 increment therebetween in 0.1% increments.

3 As noted, the nano clays are inorganic minerals with a high aspect ratio  
4 as one dimension of the particles therein falls in the nanometer range. A  
5 variety of references are available to those skilled in the art which discuss and  
6 describe nano clays suitable herein. In such regard, the clays having a plate  
7 structure and thickness of less than one nanometer are the clays of choice.  
8 The length and width of the clays may fall in the micron range. Aspect ratios  
9 of the preferred clays are in the 300:1 to 1,500: 1 range. In addition, the  
10 surface area of the exfoliated clays is preferably in the range of 700 m<sup>2</sup>/gram.  
11 Nano clays that may be suitable herein include hydrotalcite, montmorillonite,  
12 mica fluoride, octasilicate, and mixtures thereof. Nano clay is incorporated  
13 herein at a level of 1-10% (wt.) as well as any increment therebetween, in 0.1%  
14 increments.

15 Montmorillonite nano clays have a plate like structure with a unit  
16 thickness of one nanometer or less. This clay also has an aspect ratio in the  
17 1000:1 range. Because montmorillonite clay is hydrophilic, it is not  
18 compatible with most polymers and should be chemically modified to make  
19 its surface more hydrophobic. The most widely used surface treatments are  
20 ammonium cations which can be exchanged for existing cations already on the  
21 surface of the clay. The treated clay is then preferably incorporated into the  
22 polymer matrix herein, by melt mixing by extrusion, more preferably, twin-  
23 screw extrusion. In addition, at such time, and as noted above, the  
24 crosslinking promotor can also be readily combined with the clay during the  
25 melt mixing process. Those skilled in the art will therefore recognize that, in  
26 general, any type of melt mixing process can be applied to prepare the  
27 composites of the present invention, including extrusion, direct injection  
28 molding, the use of a two-roll mill, etc.

1       With regards to the development of crosslinking herein, as noted, a  
2 crosslinking promotor is employed, and preferably, the formulations herein  
3 are exposed to irradiation. Preferably, the irradiation dosage is between  
4 about 1-20 MR, as well as any numerical value and/or increment therein.

5       In addition, the polymer matrix herein may be selected from any  
6 thermoplastic or thermoset type polymer resin host. A representative  
7 thermoplastic resin herein is a nylon resin, a nylon block copolymer, nylon  
8 block copolymers containing a polyamide block and an elastomeric block,  
9 engineering thermoplastic resins (e.g., polycarbonate, polyesters,  
10 polysulphones, polyketones, polyetherimides) as well as commodity type  
11 materials (polyethylene, polypropylene, polystyrene, poly(vinylchloride))  
12 including thermoplastic elastomers. Representative thermoset materials  
13 include polyurethanes, epoxy polymers, etc.

14       In method form, the present invention relates to the steps of supplying  
15 a polymer matrix, combining said matrix with a nano clay along with a  
16 crosslinking promotor. This combination is then preferably exposed to  
17 irradiation to develop crosslinking. By the practice of such method, and as  
18 can be observed in the various working examples below, a synergistic  
19 influence of the promotor has been observed on the ability of the nano clay to  
20 improve the mechanical properties of a given polymer matrix. More  
21 specifically, in accordance with the invention herein, it has been found that  
22 should one combine a given polymer matrix with the nano clay, one will  
23 generally observe an increase in mechanical property performance, such as an  
24 increase in the flexural modulus. However, it has been found herein that  
25 upon incorporation of a crosslinking promotor, the effect of the nano clay is  
26 enhanced, in the sense that a synergy is observed as between the promotor  
27 and the nano clay on mechanical properties.

28       As a consequence of all the above, the formulations of the present  
29 invention are particularly suitable for the development of an intravascular

1 catheter having a tubular shaft comprising a nylon block copolymer and a  
2 nano clay filler, including a compound which promotes crosslinking therein,  
3 and a soft flexible tubular tip distal of and bonded to said shaft, the  
4 improvement comprising irradiation crosslinking said nylon block copolymer  
5 of said tubular shaft. The crosslinking is observed to increase the rigidity of  
6 the shaft relative to the soft distal tip.

7 In addition, the present invention also relates to a balloon type catheter  
8 having a tubular shaft comprising a nylon block copolymer and a nano clay  
9 filler, including a compound which promotes crosslinking therein, the  
10 improvement comprising irradiation crosslinking said nylon block copolymer  
11 of the balloon section.

#### 12 Working Examples

##### 13 First Experiment

14 The first experiment consisted of mixing the Nanocor 130 TGC clay  
15 and the southern Clay Closite 30B with Nylon 6 and with Nylon 6 and 3%  
16 TAIC. The Nylon 6 used with Allied's Capron B135 WP.

17 The flex modulus did increase with the use of both clays as was  
18 anticipated. The increase with the use of a crosslinking promotor was even  
19 greater, demonstrating a unique synergy as between the promotor and the  
20 nanoclay on mechanical properties. See Table I.

##### 21 Second Experiment

22 The second experiment repeated the first experiment except that the  
23 Nylon 6 was replaced by PEBAX® 72 durometer polyamide ether block  
24 copolymer. In this case just adding the nano clay did not significantly  
25 increase the flex modulus. The surprise was the increase in flex modulus  
26 when crosslinking promotors, such as TAIC, was added to the PEBAX® and  
27 nano clay. The closite 30B shows the most improvement. A second unique  
28 effect was the increase in flex modulus when the combination was  
29 crosslinked. In fact the combination of PEBAX®, Closite (nano clay) and

1 TAIC followed by crosslinking more than doubles the flex modulus. See  
2 Table II.

3 Third Experiment

4 The third experiment was similar to the first experiment noted above  
5 except the nylon-6 was replaced by nylon 12, AESNO® from Atochem. The  
6 improvements in flex modulus were much like the improvements with the  
7 PEBAX® in "Experiment Two", noted above. See Table III.

8 Fourth Experiment

9 The fourth experiment was similar to the third experiment noted  
10 above, except that nylon-12 was replaced by nylon-11, BMNO® from  
11 Atochem. The improvements in flex modulus were much like the  
12 improvements with the PEBAX® in "Experiment Two". See Table IV.

13 Fifth Experiment

14 The fifth experiment was similar to the above, except that both low  
15 density and high density polyethylene were employed as the polymer matrix.  
16 An improvement in flex modulus was again observed due to the combination  
17 of nano clay and promotor (3% wt. TAIC). See Table V.

18  
19



NYLON 6		TABLE I		CAPRON B135W					
NYLON 6	NONE	NYLON 6	NONE	NYLON 6	NONE	NYLON 6	NONE	NYLON 6	NONE
NYLON 6	NONE	NYLON 6	NONE	NYLON 6	NONE	NYLON 6	NONE	NYLON 6	NONE
NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC
NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC
NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC	NYLON 6 3% TAIC	NANO-130TC
NYLON 6	CLOSITE 30B	NYLON 6	CLOSITE 30B	NYLON 6	CLOSITE 30B	NYLON 6	CLOSITE 30B	NYLON 6	CLOSITE 30B
NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B
NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B
NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B	NYLON 6 3% TAIC	CLOSITE 30B
NYLON 6 3% TAIC	NONE	NYLON 6 3% TAIC	NONE	NYLON 6 3% TAIC	NONE	NYLON 6 3% TAIC	NONE	NYLON 6 3% TAIC	NONE
NYLON 6 3% TAIC	NONE	NYLON 6 3% TAIC	NONE	NYLON 6 3% TAIC	NONE	NYLON 6 3% TAIC	NONE	NYLON 6 3% TAIC	NONE

OMR	9,500	150	350,000
OMR	9,500	150	450,000
OMR	6,200	75	410,000
5MR	7,200	15	530,000
10MR	9,500	15	550,000
OMR	9,400	140	510,000
OMR	13,250	190	430,000
5MR	10,300	25	550,000
10MR	10,100	25	590,000
5MR	9,500	50	380,000

## PEBAX 7233

TABLE II		PEBAX 7233					
PEBAX	NONE	PEBAX	NONE	PEBAX	NONE	PEBAX	NONE
PEBAX	NONE	PEBAX	NONE	PEBAX	NONE	PEBAX	NONE
PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B
PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B
PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B
PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B	PEBAX 3% TAIC	CLOSITE 30B
PEBAX 3% TAIC	NANO-130TC	PEBAX 3% TAIC	NANO-130TC	PEBAX 3% TAIC	NANO-130TC	PEBAX 3% TAIC	NANO-130TC
PEBAX 3% TAIC	NANO-130TC	PEBAX 3% TAIC	NANO-130TC	PEBAX 3% TAIC	NANO-130TC	PEBAX 3% TAIC	NANO-130TC
PEBAX 3% TAIC	NONE	PEBAX 3% TAIC	NONE	PEBAX 3% TAIC	NONE	PEBAX 3% TAIC	NONE
PEBAX 3% TAIC	NONE	PEBAX 3% TAIC	NONE	PEBAX 3% TAIC	NONE	PEBAX 3% TAIC	NONE

8

OMR	8,000	250	105,000
OMR	7,600	200	135,000
OMR	6,500	180	160,000
5MR	6,500	75	280,000
10MR	6,500	50	275,000
OMR	9,200	300	135,000
5MR	8,200	150	200,000
10MR	7,800	125	210,000
5MR	7,900	150	150,000

NANO'S WITH XL-NYLON  
 NYLON 12  
 TABLE III

POLYMER	FILLER	FORMULATION	FILLER %	IRA DOSE	BK-STRESS	%STRAIN	FLX-MOD
NYLON 12	NONE	AESNO	0	0MR	10,000	250	200,000
NYLON 12	CLOSITE 30B	29A	5	0MR	9,000	200	200,000
NYLON 12 3% TAIC	CLOSITE 30B	28B	5	0MR	10,750	175	290,000
NYLON 12 3% TAIC	CLOSITE 30B	28B	5	5MR	10,250	75	410,000
NYLON 12 3% TAIC	CLOSITE 30B	28B	5	10MR	10,100	50	420,000
NYLON 12	NANO-130TC	#8	5	0MR	9,000	200	180,000
NYLON 12 3% TAIC	NANO-130TC	29D	5	0MR	10,200	300	200,000
NYLON 12 3% TAIC	NANO-130TC	29D	5	5MR	9,500	130	260,000
NYLON 12 3% TAIC	NANO-130TC	29D	5	10MR	9,600	125	260,000
NYLON 12 3% TAIC	NONE	29F	0	5MR	8,000	75	220,000

NANO'S WITH XL-NYLON  
 NYLON 11  
 TABLE IV

POLYMER	FILLER	FORMULATION	FILLER %	IRA DOSE	BK-STRESS	%STRAIN	FLX-MOD
NYLON 11	NONE	BMNO	0	0MR	10,000	250	170,000
NYLON 11 3% TAIC	CLOSITE 30B	28C	5	0MR	9,400	200	250,000
NYLON 11 3% TAIC	CLOSITE 30B	28C	5	5MR	9,000	125	300,000
NYLON 11 3% TAIC	CLOSITE 30B	28C	5	10MR	8,500	75	350,000

TABLE V  
NANO CLAY IN HDPE & LDPE

POLYMER	FILLER	FORMULATION	FILLER %	IRA DOSE	BK-STRESS	%STRAIN	FLX-MOD	FLX-MOD % INC
HDPE	NONE	3364	0	0MR	2,317	47	73,802	0
HDPE	CLOSITE 30B	30A	6	0MR	2,231	48	81,580	10.8
HDPE	CLOSITE 30B	30A	6	5MR	1,734	32	94,853	28.9
HDPE	CLOSITE 30B	30A	6	10MR	2,474	29	105,069	42.8
HDPE	CLOSITE 30B	30A	6	15MR	2,866	28	111,026	50.8
HDPE	CLOSITE 30B	30A	6	20MR	3,180	28	113,733	54.5
LDPE	NONE	6005	0	0MR	1,018	49	21,285	0
LDPE	CLOSITE 30B	30B	6	0MR	1,000	46	25,856	21.4
LDPE	CLOSITE 30B	30B	6	5MR	1,434	33	29,339	37.8
LDPE	CLOSITE 30B	30B	6	10MR	1,890	35	31,987	50.2
LDPE	CLOSITE 30B	30B	6	15MR	2,085	38	31,688	48.8
LDPE	CLOSITE 30B	30B	6	20MR	2,034	30	32,864	54.3

1 What is claimed is:

2 1. A polymer composite comprising a polymer matrix having,  
3 dispersed therein, a nano clay in combination with a crosslinking promotor.

4 2. The composite of claim 1, wherein said crosslinking promotor is  
5 a chemical compound which promotes crosslinking between polymer chains  
6 upon exposure to irradiation.

7 3. The composite of claim 1 wherein said crosslinking promotor is  
8 triallylisocyanurate or triallylcyanurate.

9 4. The composite of claim 1 wherein said crosslinking promotor is  
10 present at a level of about 0.5 to 10 % (wt).

11 5. The composite of claim 1 wherein said nano clay is present at a  
12 level of about 1 to 10 % (wt).

13 6. The composite of claim 1 wherein said polymer matrix is a  
14 thermoplastic polymer or thermoset polymer.

15 7. The composite of claim 1 wherein said polymer matrix is a  
16 polyamide polymer or a polyamide copolymer comprising a polyamide block  
17 and an elastomeric block.

18 8. The composite of claim 7 wherein said polyamide block is a  
19 nylon-6, nylon-6,6, nylon-11, nylon-12, copolymers of nylon-6/nylon-11,  
20 copolymers of nylon-6/nylon-12 or mixtures thereof.

21 9. The composite of claim 7 wherein said elastomeric block is  
22 selected from a polyether, polyester, hydrocarbon, polysiloxane or mixtures  
23 thereof.

24 10. A composite comprising a polymer matrix having, dispersed  
25 therein, a nano clay in combination with a crosslinking promotor, wherein  
26 said matrix is irradiation crosslinked.

27 11. A method for enhancing the mechanical properties of a polymer  
28 composite, comprising:

29 (a) supplying a polymer matrix;

1           (b) combining said matrix with a nano clay and a crosslinking  
2 promotor; and

3           (c) irradiating the combination of step (b) and crosslinking.

4           12. The method of claim 11 wherein said polymer matrix comprises  
5 polymer chains, said promotor is a chemical compound that absorbs  
6 irradiation and becomes chemically reactive to form crosslinks, and wherein  
7 said crosslinks comprise covalent bonds between said polymer chains.

8           13. The method of claim 12, wherein said irradiation is 5, 10, 15 or  
9 20 megarads.

10          14. In an intravascular catheter having a tubular shaft comprising a  
11 nylon block copolymer and a soft flexible tubular tip distal of and bonded to  
12 said shaft, the improvement comprising adding a nano clay filler and a  
13 compound which promotes crosslinking therein to said nylon block  
14 copolymer forming said shaft, and irradiation crosslinking said nylon block  
15 copolymer of said tubular shaft.

16          15. In a balloon type catheter having a tubular shaft comprising a  
17 nylon block copolymer and an integrally formed balloon section, the  
18 improvement comprising adding a nano clay filler and a compound which  
19 promotes crosslinking therein to said nylon block copolymer forming said  
20 balloon, and irradiation crosslinking said nylon block copolymer of the  
21 balloon section.

22

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/31174

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08J 3/28, 9/00, 9/06; C08K 3/34, 3/20, 3/22; C08L 23/06.

US CL : 522/83, 117, 137; 523/216, 300, 521; 524/445, 447, 449, 451; 604/96, 508, 523.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 552/83, 117, 137; 523/216, 300, 521; 524/445, 447, 449, 451; 604/96, 508, 523.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Please See Continuation Sheet

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,444,816 A (RICHARDS et al) 24 April 1984, Abstract, column 1, line 43, to column 2, line 66, column 3, lines 39-45, and Table 3.	1-15
Y	US 4,385,136 A (ANCKER et al) 24 May 1983, column 6, line 26, to column 7, line 49, column 8, lines 5-27, column 10, lines 26-37, Table II, column 11, lines 30-40, column 16, line 30, to column 17, line 10, Examples 1 and 3-6.	1-15
X	US 5,853,886 A (PINNAVAIA et al) 29 December 1998, Abstract, column 3, line 49, to column 4, line 6, column 6, line 13, to column 8, line 18, column 9, lines 4-10, column 9, lines 60-66, column 10, lines 16-26 and lines 57-65, column 13, line 64, to column 14, line 4, column 14, lines 37-47, Examples E4, E13 and E14.	1,5,6,7,10 ----- 4,11-13
---	WO 93/11190 (ALLIED-SIGNAL, INC.) 10 June 1993, Abstract, page 7, lines 8-15, column 8, lines 14-20, column 10, lines 26-30, column 21, lines 23-29, pages 23-25, page 28, lines 8-16, page 30, lines 23-29, page 33, line 28, to page 34, line 19, and Example 1.	1,5-8,10 ----- 4,11-15
Y		
A	US 4,303,595 A (ALLEN) 01 December 1981, Abstract, column 2, lines 56-61, column 3, line 61, to column 4, line 22.	14-15
Y,P	US 5,993,415 A (O,NEIL et al) 30 November 1999, Abstract, column 3, lines 37-58, and column 4, lines 37-50.	1-15

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

\* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

Date of mailing of the international search report

26 FEB 2001

Name and mailing address of the ISA/US

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/31174

## C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 5,994,445 A (KASHEL et al) 30 November 1999, Abstract, column 3, lines 14-34, column 3, line 53, to column 4, line 27.	1-15
Y,P	US 6,034,163 A (BARBEE et al) 07 March 2000, column 2, lines 22-44, column 3, lines 12-35, column 6, lines 35-61, column 7, lines 52-55.	1-15
Y,P	US 6,136,908 A (LIAO et al) 24 October 2000, Abstract and column 2.	1-15

# INTERNATIONAL SEARCH REPORT

International application No. .

PCT/US00/31174

Continuation of B. **FIELDS SEARCHED** Item3: USPAT, DERWENT, EPO, JPO: nano clay, nano fillers, nano composites, montmorillonite, hydrotalcite, mica fluoride, ostasilicate, clay, talc, mica, silicate, intercalate, nylon, polyamide, polyethylene, block copolymer